Oxidation of an *o*-tolyl phosphine complex of platinum: C-H activation and transcyclometallation.

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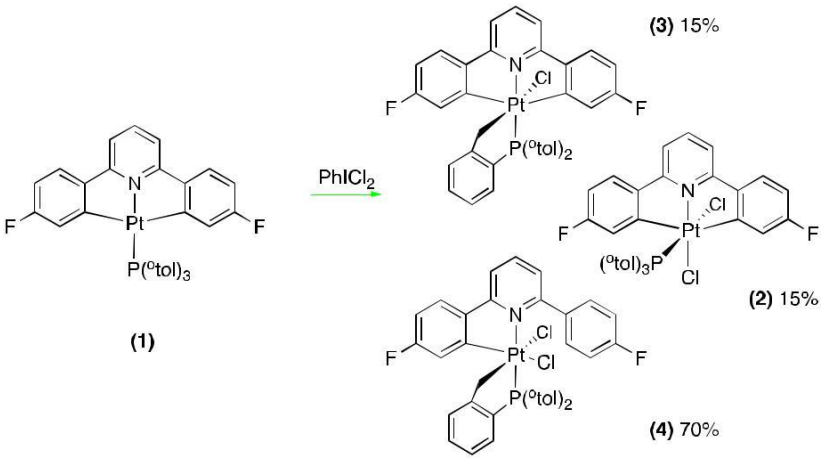


Keywords: platinum, cyclometallation, oxidation, C-H activation, transcyclometallation

Abstract

The oxidation of the tri(o-tolyl)phospine complex of the doubly cyloplatinated 2,6-di(4-fluorophenyl)pyridine ligand with the electrophilic oxidant iodobenzenedichloride was studied. Three products were formed in the ratio 15:15:70, and all were identified. The simple *cis*-dichloro platinum(IV) complex **2** (15%) remained in solution and could be purified and fully characterised. The triply cyclometallated **3** (15%), formed via the activation of a methyl group on a tolyl ring, precipitated from the reaction mixture and could not be redissolved or characterised further. Transcyclometallated **4** (70%), where one of the original cyclometallated aryl rings has exchanged for a cyclometallated phosphine ring, crystallised from the reaction mixture and was characterised crystallographically. Redissolution of **4** gave a new agostic species with the phosphine moving to a less sterically demanding position.

Introduction

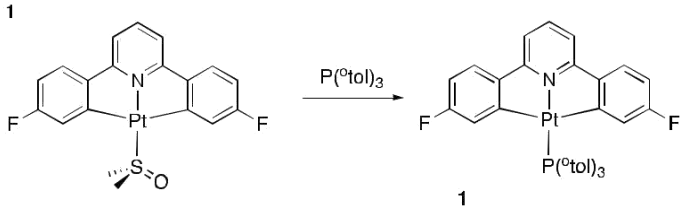
The study of platinum complexes has had a crucial role in our understanding of C-H bond activation chemistry,[1] with many studies on the mechanism of reactions.[2] The popularity of the study of platinum complexes is partly due to the amenability of study, but largely derives from the relevance of complexes to actual processes, and the ability to activate methane.[3] We have been studying oxidation reactions[4] and reductive couplings[5] at cyclometallated platinum where we have looked at the reaction of square planar platinum(II) complexes with $PhICl_2$. Oxidation with $PhICl_2$ gives an the initial delivery of a Cl^+ to the metal, generating a very electrophilic metal centre.[6] The metal would normally then react with a Cl^- to complete the oxidation and, for many complexes, the result is simply the addition of two chloride ligands to the metal centre giving an octahedral Pt(IV) centre;[4a,4c,5a,5b] which may or may not isomerise.[4a,7] However, the electrophilic metal centre can also be intercepted before it combines with chloride and significantly different reactions result when the organic groups on the ligand systems can interact with the metal centre. On occasion we have observed agostic intermediates at low temperatures (e.g. -60°C) prior to transcyclometallation[8] reactions that lead to cyclometallated alkyl phosphines.[9] With other ligands fast intra-molecular C-H activation of aromatic groups (which proceed via an electrophilic attack of the metal on an aryl ring), also at low temperature, have been observed.[4c,10] Crucial to the stability any intermediate formed is the size of the ring that is created: triphenyl phosphine can only give an unfavoured four-membered ring and no C-H activation is observed.[9b] On the other hand, a benzyl group on a phosphine ligand can lead to the formation of a favourable five-membered ring and we have recently reported on our study of such complexes: in addition to the expected electrophilic attack on the benzyl groups, we also saw a reductive coupling reaction from the newly formed metallacycle, a reaction that was ultimately identified as being reversible.[11]

In this paper, we report on our investigations into the effect of putting an tolyl group into the role of intercepting ligand and three competing reactions are observed.

Results

The synthesis of the new C^N^C platinum(II) tri(*ortho*-tolyl) phosphine complex **1** proceeds smoothly at room temperature giving product in high yield and purity, Scheme 1. The difluorinated C^N^C ligand was chosen as the NMR active ^{19}F nuclei provide a very convenient remote reporting handle on the central ^{195}Pt nucleus and do not significantly affect the chemistry.[12]

Scheme 1



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Spectroscopic data initially suggested an impure compound as there were two ^{19}F resonances (-110.23 ppm, $^{4}J_{F\text{-}Pt}$ = 33 Hz and -111.79 ppm, $^{4}J_{F\text{-}Pt}$ = 27.5 Hz), and at least twenty ^{1}H signals, including one with strong ^{195}Pt satellites at 5.73 ppm. However, a single peak in the ^{31}P NMR spectrum (17.17 ppm, $^{1}J_{P\text{-}Pt}$ = 3942 Hz) and a doublet in the ^{195}Pt NMR (–4227 ppm, $^{1}J_{Pt\text{-}P} \approx 3950$ Hz) proved that only one species was present in solution. The presence of platinum satellites on both ^{19}F peaks indicated that the C^N^C ligand was dicyclometallated and we concluded that it is the size of the phosphine, which must be too large to freely rotate (on the NMR timescale) which renders the two sides of the C^N^C group inequivalent in the NMR. This restricted rotation also affects the ^{1}H signals of the phosphine and all twelve phosphine aromatic signals appear to be separate, as are the three methyl group signals. In the ^{1}H NMR spectrum one of the protons *ortho* to Pt and F is noticeably upfield shifted at 5.73 ppm, the other seems relatively unaffected at 6.55 ppm. One of the *o*-tol aryl protons has a resonance at 8.99 ppm, compared with the rest in the range 7.7-7.1 ppm, and appears to have a weak interaction with the central platinum, as can be seen in the ^{195}Pt–^{1}H correlation spectrum.

A crystal structure, Figure 1, highlights the crowded nature of the platinum centre. One of the aromatic protons on the diphenyl pyridine (on the right-hand side in Fig 1) is pointing directly into the one of the phenyl rings of the phosphine, and is 2.70Å from the centroid of the this ring, this is presumably responsible for the ^{1}H resonance at 5.73 ppm. The other two phosphine phenyl rings have their methyl groups pointing in different directions, rendering them inequivalent. Also seen in the crystal structure is an *o*-tol aryl proton pointing directly at the Pt, with the distance being 2.87Å, presumably this has the ^{1}H resonance at 8.99 ppm.

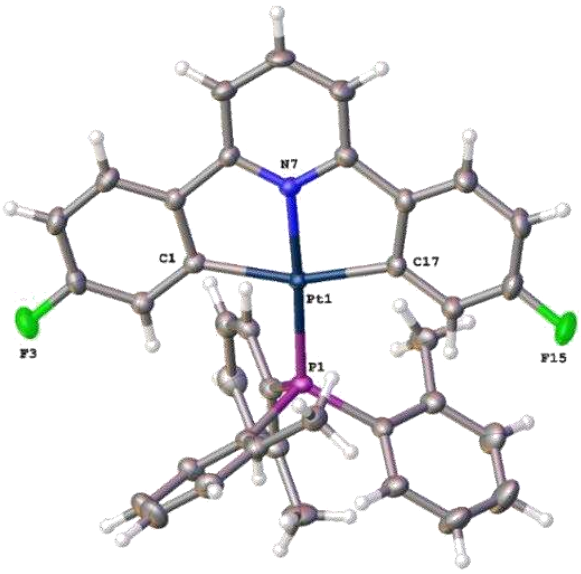
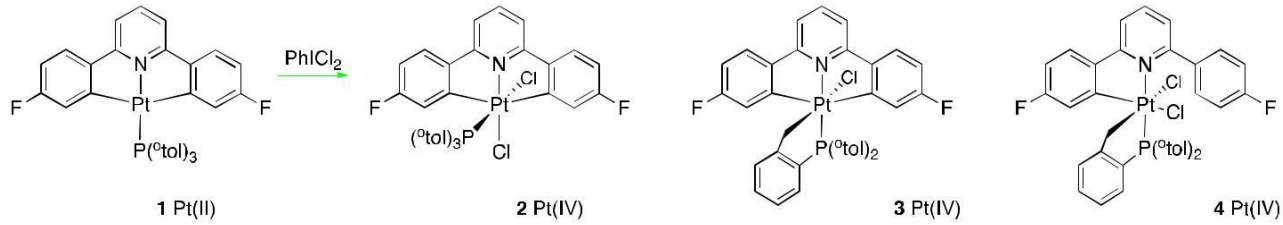


*Figure1. Crystal structure of **1**, thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Pt1-C1 2.094(3); Pt1-C17 2.085(3); Pt1-P1 2.2548(8); Pt1-N7 2.024(2); C1-Pt1-P1 97.54(8); N7-Pt1-C1 79.80(11); N7-Pt1-P1 177.32(7); N7-Pt1-C17 79.53(11); C17-Pt1-C1 158.86(12); C17-Pt1-P1 103.10(9).*

Addition of $PhICl_2$ to a chloroform solution of **1** at -40°C gave immediate and complete consumption of the starting material with the production of three new Pt(IV) complexes. The proportions of the three complexes did not seem to be affected reproducibly by reaction conditions; temperature and solvent of reaction had only little affect on product distribution. Around 15% of the product mixture was a complex that could be separated from the other two and fully characterised: it turned out to be the simple dichloro- oxidised complex **2**, Scheme 2.

Scheme 2



Pure samples of **2** were analysed; a peak at -13.96 ppm ($^{1}J_{P\text{-}Pt}$ = 2470 Hz) in the ^{31}P NMR spectrum and a doublet in the ^{195}Pt NMR spectrum at -2403 ppm indicated a Pt(IV) species.[13] A single peak in the ^{19}F NMR spectrum at -106.50 ppm ($^{4}J_{F\text{-}Pt}$ = 14 Hz) and the number of peaks present in the ^{1}H NMR spectrum indicated the C^N^C ligand remained dicyclometallated with both sides equivalent and showed that the phosphine is now able to rotate freely, suggesting that the phosphine is now *cis* to the pyridine nitrogen. A crystal suitable for X-ray crystallography was grown and confirmed the *cis* geometry, Figure 2.

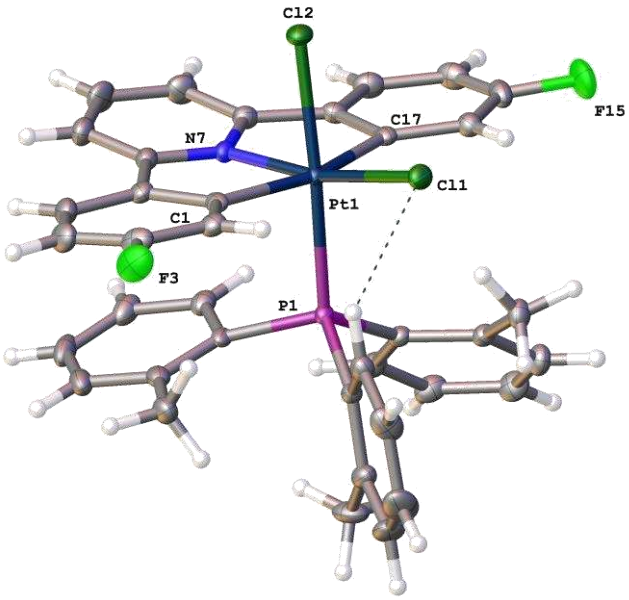


Figure 2 Crystal structure of ***2****, thermal ellipsoids drawn at 50% probability level, solvent removed for clarity. Selected bond lengths (Å) and angles (°): C1-Pt1 2.100(5); Cl1-Pt1 2.3323(18); P1-Pt1 2.3503(15); Pt1-Cl2 2.3974(15); Pt1-N7 1.985(5); Pt1-C17 2.065(7); C1-Pt1-Cl1 100.0(3); C1-Pt1-P1 91.97(17); C1-Pt1-Cl2 87.48(16); Cl1-Pt1-P1 97.53(6); Cl1-Pt1-Cl2 86.26(6); P1-Pt1-Cl2 176.21(7); N7-Pt1-C1 81.1(4); N7-Pt1-Cl1 169.29(16); N7-Pt1-P1 93.06(17); N7-Pt1-Cl2 83.15(16); N7-Pt1-C17 81.4(3); C17-Pt1-C1 162.5(4); C17-Pt1-Cl1 96.8(2); C17-Pt1-P1 90.5(2); C17-Pt1-Cl2 88.9(2).*

The remaining material consisted of two new complexes, both of which had Pt-CH_2 bonds, easily identified by the presence of ^{195}Pt satellites on alkyl ^{1}H signals. All three products were stable in solution at -60°C, with no inter-conversion or further reaction. Thus, acquisition of solution spectroscopic data was possible at low temperature and confident assignments of structure could be made. However, allowing the reaction mixture to warm to room temperature resulted in the two products with Pt-CH_2 bonds precipitating from solution. It was this behaviour that allowed the simple oxidised product **2** to be isolated in a pure form. The less abundant complex with the Pt-CH_2 bond made up a further 15 % of the product mass, and was characterised as the triply cyclometallated complex **3**. A peak in the ^{195}Pt NMR spectrum at -3028 ppm ($^{1}J_{Pt-P}$ ~ 2800 Hz) and a peak in the ^{31}P NMR spectrum at 20.26 ppm ($^{1}J_{Pt-P}$ = 2818 Hz) indicated a Pt(IV) species. The large downfield shift of the ^{31}P resonance (when compared with **2**) suggests that the phosphorus is part of a metallacycle.[14] In the ^{1}H NMR spectrum, two protons on the cyclometallated alkyl group could be seen at 2.75 ppm ($^{2}J_{H-H}$ = 13 Hz, $^{2}J_{H-Pt}$ = 74 Hz) and at 3.77 ppm ($^{2}J_{H-H}$ = 13 Hz, $^{2}J_{H-Pt}$ = 90 Hz), with the $^{2}J_{H-H}$ coupling (and COSY correlation) showing that the two protons are attached to the same carbon. Two aryl peaks with significant platinum satellites (6.18 ppm, $^{3}J_{H-Pt}$ = ~30 Hz and 5.18 ppm, $^{3}J_{H-Pt}$ = ~25 Hz) were also seen. Both the two alkyl and the two aryl protons coupled to the same ^{195}Pt nucleus. In the ^{19}F NMR, peaks at -107.52 ppm ($^{4}J_{F-Pt}$ = 28 Hz) and

-110.29 ppm ($^4J_{F\text{-}Pt}$ = 23 Hz) were seen: the presence of satellites on both peaks shows that the C^N^C ligand is still dicyclometallated.

At first sight, the notional mirror plane (vertical, as drawn in Scheme 2) through **3** should lead to only one alkyl ^{1}H resonance with Pt coupling, one aryl ^{1}H resonance with Pt coupling and one ^{19}F resonance with Pt coupling. However, the doubling of all these resonances presumably arises for a similar reason to that which complicates the NMR spectra of **1**: the bulk of the phosphine ligand. Thus, the preferred conformation will be one where the new cyclometallated ring twists out of the notional mirror plane and renders the two sides of the molecule inequivalent. With a barrier to inter-conversion that is sufficiently high, the molecule will appear to be frozen on the NMR timescale, especially at the low temperature of -40°C we were studying the reaction, giving rise to the additional resonances. While the ^{195}Pt shift and the magnitude of the $^1J_{Pt\text{-}P}$ coupling constant suggests a P-N trans arrangement, it is the doubling of the ^{1}H, and ^{19}F resonance that provides the strongest evidence for this geometry. Once precipitated, we were unable to redissolve **3** in any common solvent, rendering further study impossible.

The major component of the reaction, **4**, made up the remaining 70 % of the product mass. A doublet in the ^{195}Pt NMR spectrum at -3324 ppm is suggestive of a Pt(IV) species, with the large downfield shift (when compared to **2**) of the ^{31}P resonance to 33.21 ppm ($^1J_{P\text{-}Pt}$ = 3199 Hz) once again suggesting that the phosphorus is now part of a platinacycle. Two peaks in the ^{19}F NMR spectrum, one at -109.62 ppm with platinum satellites ($^4J_{F\text{-}Pt}$ = 43 Hz) and one at -112.68 ppm (no satellites) indicate that the C^N^C ligand is only monocyclometallated. In ^{1}H NMR spectrum there are two proton peaks for the cyclometallated alkyl group, at 4.07 ppm ($^2J_{H\text{-}Pt}$ = 76 Hz) and 4.66 ($^2J_{H\text{-}Pt}$ = 102 Hz), both on the same carbon. Thus the solution data is consistent with the structure **4** depicted in Scheme 2. With time, this species precipitated from solution, often crystallising. Crystals suitable for X-ray diffraction were isolated and the structure solved, confirming the transcyclometallated nature of the complex and the *trans* P-N geometry, Figure 3.

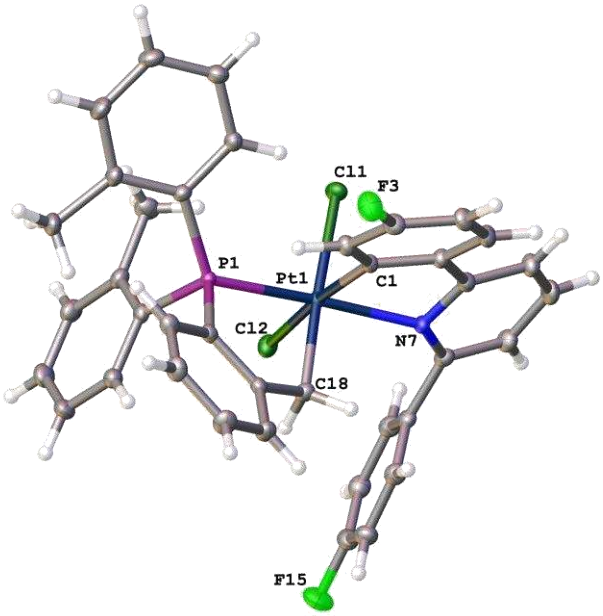
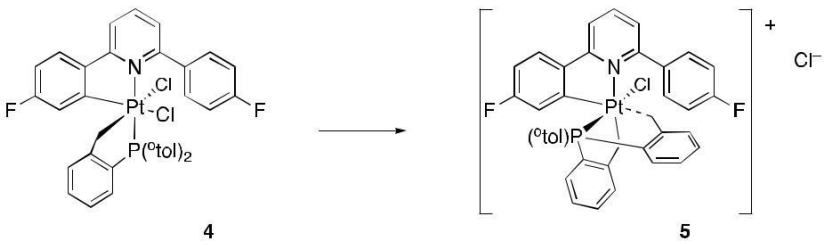


*Figure.3 Crystal structure of **4**, thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Pt1-Cl1 2.4429(6); Pt1-P1 2.2906(6); Pt1-C1 2.041(2); Pt1-Cl2 2.4086(6); Pt1-N7 2.179(2); Pt1-C18 2.075(2); P1-Pt1-Cl1 99.69(2); P1-Pt1-Cl2 90.37(2); C1-Pt1-Cl1 90.68(7); C1-Pt1-P1 96.77(7); C1-Pt1-Cl2 172.86(7); C1-Pt1-N7 80.19(9); C1-Pt1-C18 87.83(10); Cl2-Pt1-Cl1 88.15(2); N7-Pt1-Cl1 84.39(6); N7-Pt1-P1 174.99(6); N7-Pt1-Cl2 92.69(6); C18-Pt1-Cl1 177.53(8); C18-Pt1-P1 82.45(8); C18-Pt1-Cl2 93.09(8); C18-Pt1-N7 93.41(9).*

Considerable distortions away from a perfect octahedral geometry are present in the structure of **4**: while the P1-Pt1-Cl2 and C1-Pt1-Cl1 angles are less than 0.5° from an ideal 90°, the C1-Pt1-N7 angle is 80.19(9)°, the pyridine ring is canted more than 26° from the Pt-N vector and the cyclometallated aryl ring is inclined some 23.6° from the pyridine it is attached to.

We attempted to redissolve the crystals of **4** in all standard solvents, but it was only in acetone that appreciable quantities did dissolve. Even then, the redissolution was slow and appeared to be accompanied by loss of a chloride and an isomerisation. Solutions were too weak to fully characterise, but key data indicated that the phosphorous and nitrogen adopt a *cis* arrangement, allowing the bulk of the uncyclometallated o-tolyl rings to move out to a position over the plane of the original cyclometallated ligand, **5**, Scheme 3, with an agostic methyl completing the coordination sphere.

Scheme 3



Thus, solution data still shows two peaks (and only one having platinum satellites) in the ^{19}F NMR spectrum at -109.33 ppm ($^{4}J_{F\text{-}Pt}$ = 45 Hz) and -115.18 ppm, a peak in the ^{31}P NMR

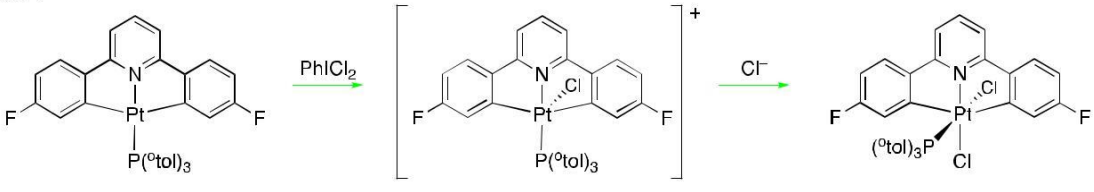
spectrum, at 23.69 ppm ($^{1}J_{P\text{-}Pt}$ = 2969 Hz) and a doublet in the ^{195}Pt NMR spectrum (-2583 ppm). In the ^{1}H NMR spectrum, the protons on the cyclometallated alkyl group are at 5.12 ppm ($^{2}J_{H\text{-}Pt}$ = 95 Hz) and 4.25 ppm ($^{2}J_{H\text{-}Pt}$ = 45 Hz) and a clear agostic interaction from one of the methyl groups (1.22 ppm) was seen in the ^{195}Pt-^{1}H correlation spectrum.

Discussion.

In several examples published by us earlier, oxidation of a C^N^C platinum phosphine complex with $PhICl_2$ initially gave a *trans* dichloride, which subsequently isomerised to the less sterically crowded and more stable *cis* isomer. Thus we have seen this behaviour for the DMSO, PMe_3, PPr_3, PBu_3, and PPh_3 analogues of **1** and have, in some cases, been able to crystallographically characterise both isomers.[9] Analogous behaviour was also seen with the addition of methyl iodide: the initial complex with the phosphine *trans* to pyridine isomerises to one in which the phosphine is *cis* to the pyridine;[5d] others have seen similar behaviour.[15] That the oxidation of **1** did not give an initial *trans* complex, and went straight to the less crowded *cis* must be a function of the sheer bulk of the tri(*o*-tolyl)phosphine. We have already seen how positioning the phosphine *trans* to the nitrogen in the square planar Pt(II) **1** results in considerable steric constraints, and presumably the addition of two additional chlorides is simply impossible with the phosphine *trans* to the pyridine, hence the direct formation of the *cis* isomer **2**. Even now, the *cis* arrangement in **2** is not completely unstrained: a N7-Pt1-Cl1 angle of 169.29(16)° is some way away from an ideal 180°.

That **2** is not the only product of the reaction is a function of the two step process by which oxidation with $PhICl_2$ takes place. As an electrophilic reagent, the first step of reaction will be the delivery of a Cl^{+} to one face of **1**, generating an unseen five-coordinate cationic intermediate. This intermediate could combine with chloride (with isomerisation) to give **2**, Scheme 4, or, more interestingly, interact with the periphery of the phosphine ligand, in this instance, a methyl group.

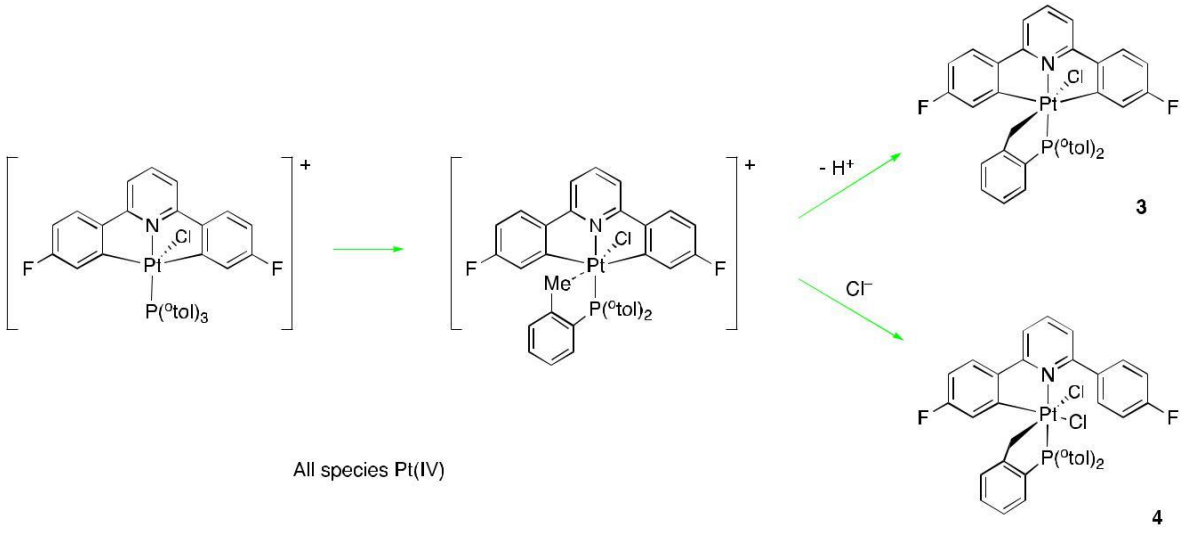
Scheme 4



1 Pt(II) Pt(IV) **2** Pt(IV)

Once the methyl group of interacts with the platinum centre, two possibilities present themselves. Firstly the methyl group could be directly deprotonated with concomitant formation of a C-Pt bond to give tricyclometallated **3** or, secondly, a methyl proton could be

transferred in a transcyclometallation[8] reaction to one of the original cyclometallated aryl groups, together with combination with the final chloride to give **4**, Scheme 5.



Previously we have worked with alkyl phosphines, where only the second, transcyclometallation, pathway was observed (with the relief of strain associated with the fused cyclometallated rings of the C^N^C ligand being partially responsible for driving the reaction).[9] This behaviour might be expected, given that the high pKa of an alkyl group suggests direct deprotonation is not a viable reaction pathway. The pK_a of the tolyl-Me protons is around 40, about 20 units lower than an alkyl chain, due to resonance effects from the aryl ring, and this reduction in pKa must be sufficient to now render the deprotonation a viable reaction pathway, hence the formation of some **3**. However, the reduction in pKa is clearly not enough to make this the exclusive or indeed, dominant, pathway as the majority of the reaction did indeed follow the transcyclometallation route.

We should at this point compare our proposed intermediate with the agostic complex **5** that forms upon redissolution of **4**, Scheme 3. That the agostic methyl in **5** is stable enough in solution at room temperature to be identifiable, as it does not undergo a second transcylometallation reaction, is not unexpected: their would be no relief of strain helping to drive the transcyclometallation reaction. So the non-deprotonation of the agostic methyl in **5** reinforces our point above about the pKa of the methyl: it is still too high for pathways involving deprotonation to represent readily accessible reaction routes, but is low enough to be viable under certain circumstances. Thus we can conclude the course of our oxidation reaction must be finely balanced and, presumably, it ought to be able to influence the outcome under appropriate conditions. We had limited scope for changing reaction conditions, with neither reaction temperature (-60°C to +20°C) or reagent concentration having any effect on product distribution.

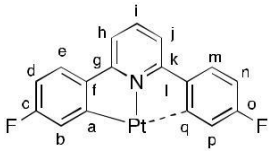
Conclusions

The products of the oxidation of the tri(*o*-tolyl)phosphine complex of the C^N^C doubly cycloplatinated diphenylpyridine ligand with iodobenzene dichloride are consistent with electrophilic attack by the oxidant, giving an unseen five-coordinate intermediate. Three pathways of reactivity are seen from this intermediate: simple combination with a chloride, electrophilic attack on a methyl group, and transcyclometallation. We were unable to control the relative proportions of the products, but the evidence would suggest that each pathway is independent of the others, and essentially irreversible.

Experimental

General

All chemicals were used as supplied, unless noted otherwise. All NMR spectra were obtained on a Bruker Avance 400, 500 or 600 MHz spectrometers and were recorded at room temperature, in chloroform, unless stated otherwise. ^{1}H and ^{13}C signals are referenced to external TMS, assignments being made with the use of decoupling, GOESY and COSY pulse sequences. ^{1}H-^{19}F, ^{1}H-^{31}P and ^{1}H-^{195}Pt correlation spectra were recorded using a variant of the HMBC pulse sequence. ^{19}F and ^{31}P chemical shifts are quoted from the directly observed signals (referenced to external $CFCl_3$ and 85% H_3PO_4, respectively) whereas the ^{195}Pt chemical shifts quoted are taken from the 2D HETCOR spectra (referenced to external Na_2PtCl_6). Starting platinum complex DMSO was prepared as previously reported.[16] The following labelling scheme was used for the complexes:



Synthesis of complex 1

To a solution of [(2,6-di(4-fluorophenyl)pyridine)Pt(DMSO)] (100 mg, 1.86 x10^{-4} mol) in chloroform at room temperature was added a chloroform solution of tri(o-tolyl)phosphine (62 mg, 2.05 x10^{-4} mol, 1.1 equiv). The mixture was stirred for five minutes before solvent and liberated DMSO were removed under high vacuum. Column chromatography (chloroform on silica) was used to purify the product. Yields: 136 mg (1.79 x10^{-4} mol, 96%).

δ_H = 8.99 (1H, dd, $^{3}J_{H\text{-}H}$ = 16 Hz, $^{3}J_{H\text{-}H}$ = 8 Hz, H_{Ar})*, 7.67 (1H, dd, $^{3}J_{H\text{-}H}$ = 11 Hz, $^{3}J_{H\text{-}H}$ = 8 Hz, H_{Ar}), 7.63 (1H, dd, $^{3}J_{H\text{-}H}$ = 8 Hz, H_i), 7.23-7.47 (9H, m, H_{Ar}) 7.41 (1H, H_e), 7.38 (1H, H_m), 7.26 (2H, dd, $^{3}J_{H\text{-}H}$ = 8 Hz, $H_{h,j}$), 7.14 (2H, m, H_{Ar}), 6.62 (1H, dt, $^{3}J_{H\text{-}H}$ = $^{3}J_{H\text{-}F}$ = 8 Hz, ^{4}J = 2 Hz, H_d), 6.58 (1H, dt, $^{3}J_{H\text{-}F}$ = $^{3}J_{H\text{-}H}$ = 8 Hz, ^{4}J = 2 Hz, H_n), 6.55 (1H, dd, $^{3}J_{H\text{-}F}$ = 11 Hz, $^{4}J_{H\text{-}H}$ = 2 Hz, $^{3}J_{H\text{-}Pt}$ = 29 Hz, H_p), 5.73 (1H, dd, $^{3}J_{H\text{-}F}$ = 11 Hz, $^{4}J_{H\text{-}H}$ = 2 Hz, $^{3}J_{H\text{-}Pt}$ = 26 Hz, H_b), 2.99 (3H, s, Me), 1.88 (3H, s, Me), 1.75 (3H, s, Me) ppm.

*Shows a correlation to platinum in the ^{1}H-^{195}Pt HMBC spectrum when the experiment is optimised for long range coupling.

δ_C = 22.19 (d, $^{4}J_{C\text{-}P}$ = 9 Hz,C_{Me}), 23.39 (d, $^{4}J_{C\text{-}P}$ = 4 Hz,C_{Me}), 25.03 (d, $^{4}J_{C\text{-}P}$ = 9 Hz, C_{Me}),110.27 ($C_{d,n}$), 114.27, (C_{Ar}), 121.29 (d, $^{4}J_{C\text{-}P}$ = Hz, $^{4}J_{C\text{-}P}$ = Hz, H_b), 124.72-125.75 ($C_{h,j,p,Ar}$), 125.75-127.00 ($C_{g,k,Ar}$) 133.15 ($C_{e,m}$), 140.12 (C_i), 143-147 ($C_{f,l,Ar}$) 144.56 (C_{Ar}), 162.89-165.36 ($C_{c,o,Ar}$) 167.78 (m, $C_{a/q}$) 170.74 (m, $^{1}J_{C\text{-}H}$ = 737 Hz, $C_{a/q}$) ppm.

δ_F = -110.23 ($^{4}J_{Pt\text{-}F}$ = 32.5 Hz), -111.79 ($^{4}J_{Pt\text{-}F}$ = 27.5 Hz) ppm. δ_P = 17.17 ($^{1}J_{P\text{-}Pt}$ = 3942 Hz) ppm. δ_{Pt} = -4227 (d, $^{1}J_{Pt\text{-}P}$ = ~3800 Hz) ppm.

HR-MS (ESI): found 764.1784, calculated 764.1784 = $C_{38}H_{30}F_2N^{194}PtP$ $[M]^+$.
Crystals suitable for Xray analysis were grown by the slow evaporation of solvent from a chloroform solution, Table 1.

Synthesis of complexes 2, 3 and 4

To a chloroform (10 ml) solution of **1** (20 mg, 2.6 $x10^{-5}$) was added $PhICl_2$ (10 mg, excess) at -40 °C giving full conversion to complexes **2**, **3** and **4** (15, 15, 70% respectively by NMR integration). Allowing the reaction mixture to warm to room temperature led to the precipitation of **3** and **4**. Complex **2** was recovered by filtering the mixture and removing the solvent; additional purification was by column chromatography, loading on a silica column with chloroform and eluting with ethyl acetate (3 mg, 3.7 $x10^{-6}$ mol, 14%)

Complex 2

δ_H = 7.69 (2H, dd, $^3J_{H-F}$ = 8 Hz, $^4J_{H-H}$ = 2.5 Hz, $^3J_{H-Pt}$ = 19 Hz, H_b), 7.42 (1H, t, $^3J_{H-H}$ = 8 Hz, H_i), 7.31 (2H, dd, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-F}$ = 5 Hz, H_e), 7.18 (3H, m, H_l), 7.10 (3H, m, H_m), 7.01 (2H, d, $^3J_{H-H}$ = 8 Hz, H_h), 6.96 (3H, m, H_k), 6.85 (3H, m, H_n), 6.64 (2H, td, $^3J_{H-F}$ = $^3J_{H-F}$ = 8.5 Hz, $^4J_{H-H}$ = 2.5 Hz, H_d), 1.37 (9H, s, H_p) ppm.
δ_C = 22.76 (d, $^3J_{C-P}$ = 4 Hz, C_p), 122.32 (d, $^2J_{C-F}$ = 24 Hz, C_d), 116.19 (s, $^3J_{C-Pt}$ = 30 Hz, C_h), 121.85 (d, $^2J_{C-F}$ = 20 Hz, C_b), 124.78 (d, $^2J_{C-P}$ = 12 Hz, C_k), 127.03 (d, $^3J_{C-F}$ = 9 Hz, C_e), 129.05 (s, C_l), 131.54 (s, C_m), 132.86 (d, $^3J_{C-P}$ = 10 Hz, C_n), 140.37 (s, C_i), 121.94 (d, $^4J_{C-F}$ = 2 Hz, C_f), 143.28 (m, C_j), 162.08 (s, C_g), 163.93 (m, C_a), 164.13 (d, $^1J_{C-F}$ = 260 Hz, C_c) ppm.
δ_F = -106.5 ($^4J_{F-Pt}$ = 14 Hz) ppm. δ_P = -13.96 ($^1J_{P-Pt}$ = 2470 Hz) ppm. δ_{Pt} = -2403 (d, $^1J_{Pt-P}$ ~ 2500 Hz) ppm.

HR-MS (ESI): found 798.1397, calculated 798.1394 = $C_{38}H_{30}F_2PN^{194}Pt$ = $[M-Cl]^+$.
Crystals suitable for X-ray analysis were grown by the slow evaporation of solvent from a chloroform solution, Table 1.

Complex 3

δ_H = 9.08 (dd, $^3J_{H-P}$ = 16 Hz, $^3J_{H-H}$ = 9 Hz, H_{Ar}), 6.18 (d, $^3J_{H-F}$ =11 Hz, $^3J_{H-Pt}$ = ~30 Hz, H_b), 5.18 (d, $^3J_{H-F}$ =10 Hz, $^3J_{H-Pt}$ = ~25 Hz, H_b), 2.75 (d, $^2J_{H-H}$ = 13 Hz, $^2J_{H-Pt}$ = 74 Hz, CH_2), 3.77 (d, $^2J_{H-H}$ = 13 Hz, $^2J_{H-Pt}$ = 90 Hz, CH_2) ppm.
δ_F = -107.52 ($^4J_{F-Pt}$ = 28 Hz), -110.29 ($^4J_{F-Pt}$ = 23 Hz) ppm. δ_P = 20.26 ($^1J_{P-Pt}$ = 2818 Hz) ppm. δ_{Pt} = -3028 (d, $^1J_{Pt-P}$ = ~2900 Hz) ppm.

Complex 4

δ_H = 8.55 (dd, $^3J_{H-P}$ = 17 Hz, $^3J_{H-H}$ = 8 Hz, H_{Ar}), 5.92 (d, $^3J_{H-F}$ =11 Hz, $^3J_{H-Pt}$ = 39 Hz, H_b), 4.07 (d, $^2J_{H-H}$ = 12 Hz, $^2J_{H-Pt}$ = 76 Hz, CH_2), 4.66 (d, $^2J_{H-H}$ = 12 Hz, $^2J_{H-Pt}$ = 102 Hz, CH_2) ppm.
δ_F = -109.62 ($^4J_{F-Pt}$ = 43 Hz) -112.68 ppm. δ_P = 33.21 ($^1J_{P-Pt}$ = 3199 Hz) ppm. δ_{Pt} = -3324 (d, $^1J_{Pt-P}$ = ~2900 Hz) ppm.

Crystals suitable for X-ray grew from the reaction mixture, Table 1.

Synthesis of Complex 5

Crystals of **4** were stirred in d_6-acetone until (approx. 3 weeks) sufficient was dissolved to record solution data.

Complex 5

δ_H (Acetone-d_6) = 6.54 (dd, $^2J_{H\text{-}F}$ = 7 Hz, $^3J_{H\text{-}Pt}$ = 52 Hz, H_b), 5.12 (d, $^2J_{H\text{-}H}$ = 13.5 Hz, $^2J_{H\text{-}Pt}$ = 95 Hz, C*H*$_2$), 4.25 (d, $^2J_{H\text{-}H}$ = 13.5 Hz, $^2J_{H\text{-}Pt}$ = 45 Hz, C*H*$_2$) 1.86 (3H, s, Me), 1.22 (3H, s, Me)* ppm. *Correlation to platinum seen, though satellites not visible.

δ_F (Acetone-d_6) = -109.33 ($^4J_{F\text{-}Pt}$ = 45 Hz), -115.18 ppm. δ_P (Acetone-d_6) = 23.69 ($^1J_{P\text{-}Pt}$ = 2969 Hz) ppm. δ_{Pt} (Acetone-d_6) = -2583 (d, $^1J_{Pt\text{-}P}$ = ~3000 Hz) ppm.

A large (relative to background) peak in the electrospray mass spectrum suggests a cationic species. HR-MS (ESI): found 798.1396, calculated 798.1394 = $C_{38}H_{30}F_2PN^{194}Pt$ = $[M]^+$.

Table 1: Xray data for the complexes

Complex	**1**	**2**	**4**
Crystal form	yellow block	colourless block	colourless block
Dimensions/mm	0.2 × 0.18 × 0.12	0.2 × 0.18 × 0.03	0.3 × 0.2 × 0.06
Emp. Formula	$C_{39}H_{31}Cl_3F_2NPPt$	$C_{38}H_{30}Cl_2F_2NPPt$	$C_{41}H_{36}Cl_2F_2NOPPt$
Mw	884.06	835.59	893.67
Crystal system	monoclinic	monoclinic	triclinic
Space group	C2/c	$P2_1/n$	P-1
a/Å	36.4648(9)	10.92104(15)	9.33343(14)
b/Å	8.3932(2)	15.5683(2)	12.19811(14)
c/Å	23.2143(7)	18.6739(3)	16.57528(15)
α/°	90	90	99.8343(9)
β/°	104.094(3)	95.5114(15)	105.1171(10)
γ/°	90	90	101.2367(11)
U/Å^3	6891.0(3)	3160.30(8)	1737.24(4)
T/K	150(2)	150(2)	150(2)
Z	8	4	2
D_{calc}/Mg m^{-3}	1.704	1.756	1.708
F(000)	3472.0	1640.0	884.0
μ(MoKα)/mm^{-1}	4.392	4.701	4.284
θ max/°	31.29	30.891	31.497
Refl. Measured	27581	42117	97999
Unique data	10276	9104	11081
*R*1 [$I > 2\sigma(I)$]	0.0321	00232	0.0216
*wR*2	0.0677	0.0437	0.0691
Data/rest/param	10276/0/464	9104/0/409	11081/0/446

Supporting Information

Full details and discussions of the Xray structures are available. CIF files are also available to download from the CCDC, reference numbers: 1565876-1565878.

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